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In re Application of: Mahmud, et al.

Application No.: 09/975,699

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For: A METHOD OF MAKING A MULTI-PHASE AGGREGATE USING A MULTI-STAGE PROCESS

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Amendment  
U.S. Patent Application No. 09/975,699

Accordingly, the applicants respectfully request reconsideration of the references not previously considered by the Examiner.

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## CARBON-SILICA DUAL PHASE FILLER: PART IV. SURFACE CHEMISTRY

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### ABSTRACT

A method for estimating the amount of functional groups on the carbon-silica dual phase fillers (CSDPF) available to react with organosilane coupling agents is reported. The method employs trimethylchlorosilane (TMCS) as an analytical probe, and involves equilibrating the samples with TMCS in toluene. The amount of TMCS that reacts with the surface functional groups is obtained by monitoring the concentration of reactants and products of the reaction by Gas Chromatography Mass Spectrometry. The amount of TMCS reacted with the fillers' surface functional groups is compared to the pH, and the active hydrogen content as measured by  $\text{LiAlH}_4$ . Comparison of these measures with the CSDPF, carbon blacks and a fumed silica sample is provided.

The dual phase fillers have a heterogeneous surface, containing both carbon and silica phases. Multipoint BET nitrogen surface area is used in combination with iodine number to estimate the individual carbon and silica phase surface areas. From this, the packing density of the trimethylsilyl group attached to the silica phase of the CSDPF surface was estimated and compared to silica.

Silanols on these dual phase fillers were detected by infrared spectroscopy. The infrared band for silanols is located at  $975\text{ cm}^{-1}$ . The absorbance of this band is shown to correlate with TMCS uptake and diminish after reaction with TMCS, suggesting that silanols indeed are participating in the uptake of TMCS.

### INTRODUCTION

This is part four in a series of articles on the Carbon-Silica Dual Phase Fillers (CSDPF), a new generation of materials for rubber reinforcement. The first two papers introduced this new material, reviewing the reasons for its development and providing an overview of its analytical and in-rubber performance properties.<sup>1,2</sup> The third paper described in detail the analytical characterization of these new materials using electron spectroscopy for chemical analysis (ESCA) and infrared spectroscopy (IR).<sup>3</sup>

In the first paper it was established that this new material was similar in morphology to carbon black comprised, however, of individual composite aggregates containing carbon and silica phases (a dual phase aggregate). The dual phase fillers were shown to have higher polymer-filler interaction than a blend of silica and carbon black of equivalent silicon content. The dual phase fillers were also shown to have lower filler-filler interaction in comparison to either conventional carbon black or silica of comparable surface area. As a result it was conjectured that the dual phase fillers would require less coupling agent to bring about the same level of hysteresis as silica compounds. This was subsequently confirmed.<sup>2</sup> The second paper in this series reported on an in-depth study of the dual phase fillers in relation to compounding design and mixing techniques for application to passenger and truck tire tread compounds. It was revealed that with proper mixing and compound formulations, the dual phase fillers can provide an improved balance of hysteresis with increased abrasion resistance when compared to carbon black and silica compounds.

In the third paper of this series, spectroscopic analysis of these dual phase fillers was discussed.<sup>3</sup> ESCA and infrared spectroscopy demonstrated that the principle silicon species present in the dual phase fillers is silica, which is intimately distributed with the carbon phase of the dual phase filler particles. Consequently the dual phase fillers can be thought of as composite aggregates containing carbon and silica phases, hence, dual phase aggregates. The silica phases in the dual phase fillers were thought to be similar in surface chemistry to silica, which would suggest silanols on the surface.

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It is known that the surface modification of a filler by coupling agents plays a very important role in increasing the polymer-filler interaction and depressing filler-filler interaction, which has a positive impact on dynamic properties of the filled vulcanizate.<sup>1</sup> It is also known that the reactivity of the coupling agent towards a filler is determined by the surface chemistry of the filler, especially the nature, concentration, and distribution of the functional groups. With regard to the silane coupling agents, which have been demonstrated to be very efficient in reacting with rubber fillers, the functional groups on the silica surface responsible for coupling have been identified as silanols.<sup>4-6</sup> It has been conjectured that some of the oxygen containing groups on carbon black would participate in this coupling. Accordingly, knowledge of the surface chemistry of these dual phase fillers is important to understanding the polymer-filler, filler-filler interactions, and the amount of functional groups available to react with the coupling agents.

Since silica is one of the phases on the surface of the dual phase fillers, it is important to understand the amount of silanols that are available for coupling reactions. There are a number of methods for measuring the silanol content on silicas, such as reactions with organometalics or metal hydrides,<sup>7-9</sup> measurement of weight loss up to 1100 °C,<sup>10</sup> reaction with organosilanes,<sup>11-13</sup> infrared spectroscopy,<sup>14,15</sup> nuclear magnetic resonance,<sup>16,17</sup> and chemical reactions in combination with spectroscopic analysis.<sup>18-22</sup> Reaction with organometalics, metal hydrides and mass loss on heating are not amenable to the dual phase filler because of interferences from functional groups on the carbon phase that may not participate in reactions with the coupling agent. Also spectroscopic methods will measure for example, total silanols, not the functional groups that are available to react only with coupling agents. This is a result of the size of the coupling agent, which sterically interferes with a complete reaction of these surface functional groups.

Trimethylchlorosilane (TMCS) was chosen as a chemical probe to measure the amount of surface functional groups on the dual phase fillers available to react with an organosilane coupling agent, such as bis(3-triethoxysilylpropyl)-tetrasulphane (TESPT), because TMCS is very reactive to silanols, and its reaction with silica surfaces has been well established.<sup>23-29</sup> Since the trimethylsilyl group is smaller than the triethoxy group on TESPT, it is expected that the amount of functional groups measured using TMCS would be an upper bound estimate of functional groups available to participate in the coupling reaction with such silane coupling agents.

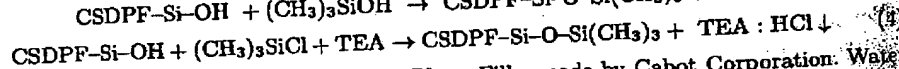
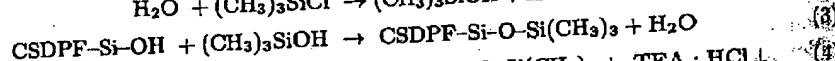
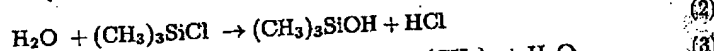
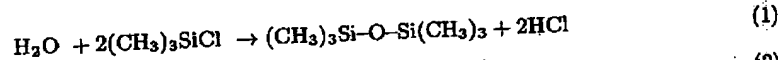
In this paper the amount of functional groups on the fillers available to participate in the coupling reaction has been estimated using the uptake of TMCS. The amount of TMCS uptake on these samples is compared to the active hydrogen content, as measured by  $\text{LiAlH}_4$ , and pH. Infrared spectroscopy was used to identify the type of functional groups on these materials as well as to provide information regarding the nature of the interaction between the surface functional groups and TMCS.

## EXPERIMENTAL

The general analytical properties of the carbon-silica dual phase fillers, carbon black, silica and treated samples used in this study are given in Table I.

### TMCS UPTAKE

The reactions of TMCS with surface silanols and water (remaining after drying) can be expressed as follows:



CSDPF is an acronym for Carbon-Silica Dual Phase Filler made by Cabot Corporation. Water in the system reacts rapidly with TMCS to form trimethylsilanol (TMS-OH) and hexamethyldisiloxane (HMD) according to reactions 1 and 2.<sup>30</sup> The proportion of these products formed is dependent on pH<sup>31</sup>; the presence of acid favors the condensation to form HMD whereas a neutral

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TABLE I  
TYPICAL ANALYTICAL PROPERTIES OF CARBON-SILICA DUAL PHASE FILLERS,  
CARBON BLACKS, SILICA AND TREATED SAMPLES

Sample <sup>a</sup>	Silicon Content, %	BET <sup>b</sup> Nitrogen Surface Area, m <sup>2</sup> /g	External Surface Area (STSA), m <sup>2</sup> /g	CDBP <sup>c</sup> mL/100 g
CSDPF-A	4.84	154.3	121.4	100
CSDPF-E	5.73	210.8	136.7	104
CSDPF-F	3.20	102.6	87.1	103
N234	0.01	122.2	120.4	101
N134	0.08	172.2	145.9	102
HF-CSDPF-A	0.72	310.1	154.8	—
HNO <sub>3</sub> -CSDPF-A	3.8	244.3	120.3	—
H <sub>2</sub> O-CSDPF-A	2.1	234.8	138.6	—
Fumed Silica	NA	318.3	253.8	—

<sup>a</sup> CSDPF-A is ECOBLACK<sup>TM</sup> CRX<sup>TM</sup> 2000. HF-CSDPF-A is HF treated CSDPF-A. HNO<sub>3</sub>-CSDPF-A is nitric acid treated CSDPF-A. H<sub>2</sub>O-CSDPF-A is water Soxhlet extracted CSDPF-A. Fumed silica is CAB-O-SIL<sup>®</sup> HS-5. ECOBLACK<sup>TM</sup> is a trademark of Cabot Corporation. CRX<sup>TM</sup> is a trademark of Cabot Corporation. CAB-O-SIL<sup>®</sup> is a registered trademark of Cabot Corporation.

<sup>b</sup> BET is multipoint nitrogen surface area using the BET theory (ASTM D 4820).

<sup>c</sup> CDBP is *n*-butyl phthalate absorption number of compressed sample (ASTM D 3493).

environment favors the formation of trimethylsilanol.<sup>30</sup> The HMD produced does not react with silanol groups,<sup>12</sup> and we have found it not to adsorb onto the dual phase filler surfaces under the conditions used in this work. Consequently HMD is a viable species to monitor the amount of water that has reacted with TMCS, whose product does not react with surface silanols. The trimethylsilanol (TMS-OH) formed reacts in a condensation like fashion with some of the surface silanols as shown in reaction 3.<sup>32</sup> TMCS also reacts directly with surface silanols according to reaction 4,<sup>12</sup> particularly in the presence of amines.<sup>33</sup>

The TMCS uptake was determined by measuring the reduction in concentration of TMCS and adjusting for the amount of HMD gained. At this juncture the amount of TMS-OH remaining in solution was not used in the correction, however, its presence was monitored and had been estimated to be low relative to TMCS uptake. As will be shown later, the TMCS uptake on this silica sample is in good agreement with literature values.

In general, this method involves equilibrating the samples, as a slurry in toluene, with TMCS. Triethylamine (TEA) was added to catalyze the reaction of TMCS with the silanols. The samples were allowed to equilibrate for sixteen hours. The concentrations of TMCS and HMD in solution were determined using a Gas Chromatography Mass Spectrometer (GC-MS). Since TMCS is very reactive, solutions containing it were first treated with methanol to convert the TMCS to trimethylmethoxysilane (TMMS), prior to GC analysis.

**Dry box.**—Because of the reactivity of TMCS with water, all analytical manipulations were carried out in a polypropylene dry box containing an argon atmosphere, maintaining a water content of less than 550 ppm. The moisture content was monitored using a dew point meter (Panadry Hygrometer, Panametrics, Inc., Waltham, MA.). To minimize weighing errors due to static electricity in the dry atmosphere, an ionizing bar was employed (Ionizing Bar and Automatic Ion Watch from Terra Universal, Inc.) Samples were dried at 150 °C for 16 hours under a flowing stream of argon. The TMCS and HMD stock solutions were prepared in a glove bag and then transferred to the dry box, to minimize contamination of the dry box with these relatively heavy vapors.

**Glassware.**—All glassware was silanized using neat trimethylchlorosilane to cap the surface silanols on the walls of the glassware. The glassware was then rinsed with toluene and acetone followed by drying for one hour at 125 °C, except for volumetric glassware which were dried by purging with nitrogen gas. Polypropylene caps were used with Teflon-silicone liners with the Teflon side always facing the liquid.

**Gas Chromatograph-Mass Spectrometer.**—The instrument used was a Hewlett Packard HP5890 Gas Chromatography equipped with a HP 5970 Mass Selective Detector, a HP 7673 Injector equipped with a straight 4 mm glass liner with a large plug of glass wool (all silanized with 10% trimethylchlorosilane in toluene and then baked in a furnace in air at 500 °C for 30 minutes prior to installation), and a HP 7673A Autosampler. The column was a HP-5M.S., 30 meter by 0.25 mm ID with 0.25 micron phenylsilicon polymer film. The carrier gas was helium with a split flow of 200 mL/min with a column pressure of 20 K Pa. This results in a column flow of approximately 1 mL/min and about a 200 to 1 split ratio. One microliter of sample was injected onto the column. The Mass Selective Detector (electron impact) was operated in Selective Ion Monitoring mode with a source voltage of 1800. Figure 1 contains an example chromatogram. The fragment ions and approximate retention times were as follows: methanol ( $m/z$  31,  $rt$  1.56 min) is  $\text{CH}_2\text{OH}^+$ , trimethylsilanol ( $m/z$  75,  $rt$  1.77 min) is  $(\text{CH}_3)_2\text{SiOH}^+$ , trimethylmethoxysilane ( $m/z$  89,  $rt$  1.77 min) is  $(\text{CH}_3)_2\text{SiOCH}_3^+$ , trimethylchlorosilane ( $m/z$  93,  $rt$  1.79) is  $(\text{CH}_3)_2\text{SiCl}^+$ , hexane ( $m/z$  57,  $rt$  1.88 min) is  $\text{CH}_3(\text{CH}_2)_5^+$ , and hexamethyldisiloxane ( $m/z$  147,  $rt$  2.21 min) is  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3^+$ . The tiny peak before hexane was an unidentified impurity in one of the solvents or reagents. Trimethylsilanol, methanol and TMCS were monitored for diagnostic purposes.

**Preparation of samples.**—The samples were first milled with a mortar and pestle and then dried at 125 °C in the laboratory oven outside of the dry box for two hours. The dried samples were allowed to cool in a desiccator and then transferred into the drybox. The samples were weighed into the reaction vials (5 mL centrifuge tubes) inside the dry box, typically 0.02 to 0.2 grams depending on the anticipated silanol content. These vials containing the samples were then dried, in an oven which was in the dry box, for sixteen hours under an argon stream at 150 °C. The samples were taken out of the oven while hot and only when the moisture content in the dry box was 550 ppm or less. The vials were then capped and allowed to cool to ambient temperature inside of the dry box prior to adding reagents to the samples.

**Reagents and solvents.**—Trimethylchlorosilane, triethylamine, hexane, toluene and methanol were obtained from Aldrich Chemical, Milwaukee, WI 53201. Hexamethyldisiloxane was obtained from United Chemicals Technologies, Bristol, PA 19007. Triethylamine, toluene and hexane were stored over 3A molecular sieves.

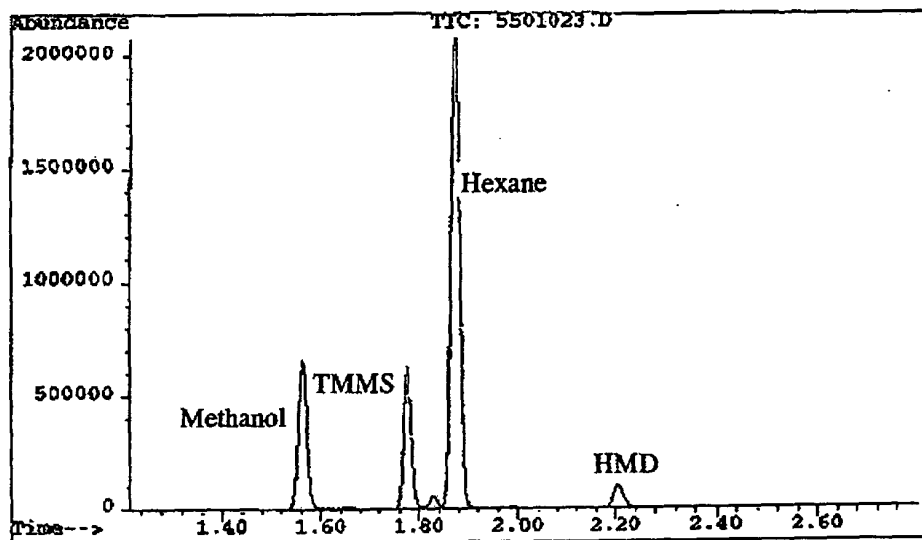


FIG. 1.—Example of a total ion chromatogram obtained using a gas chromatograph mass spectrometer.

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**Reactions.**—All stock solutions were prepared using 1% hexane in toluene. To the reaction vials containing the pre-weighed and dried samples, 1 mL of TMCS stock solution (3.0 mg/mL, 0.028 mmole/mL) was added and allowed to equilibrate for two hours with shaking. Then 1 mL of the triethylamine stock solution (5.6 mg/mL, 0.055 mmole/mL) was added to all the vials and allowed to equilibrate by shaking for approximately 16 hours. The TMCS standards and the samples were treated in a like manner. At the end of the 16 hour equilibration, 2 mL of methanol stock solution (1.82 mg/mL, 0.057 mmole/mL) was added to all vials and allowed to equilibrate for 1.5 hours prior to GC-MS analysis.

**Calibration curves.**—The calibration curve for TMCS was constructed in the form of trimethylmethoxysilane (TMMS) by taking the GC-MS peak area ratios of trimethylmethoxysilane to hexane versus concentration of TMCS. Hexane was used as an internal standard. The concentration of the TMCS calibration solutions was calculated based on serial dilutions from the stock solution. The concentration of the TMCS stock solution was based on the gravimetric amount of TMCS used in the preparation. The calibration curve for hexamethyldisiloxane (HMD) was obtained by taking the GC-MS peak area ratios of HMD to hexane versus concentration of HMD, which was prepared by dilutions from a stock solution. For both calibration curves a second order polynomial equation was used.

**TMCS uptake calculation.**—The following equation was used to calculate the amount of TMCS that reacts with the samples along with a correction for the measured amount that reacts with water whose product do not react with the samples, otherwise known as TMCS uptake (mmoles/g).

$$\text{TMCS Uptake} = ([\text{TMCS}]_{\text{loss}} - 2 \cdot [\text{HMD}]_{\text{gain}}) / [\text{Sample}] \quad (5)$$

$[\text{HMD}]_{\text{gain}}$  is the concentration of HMD found (in mmole/mL) in the sample vials minus that found in the blank vials.  $[\text{TMCS}]_{\text{loss}}$  is the concentration of TMCS (mmole/mL) in the high concentration TMCS standard vial minus the concentration of TMCS in the sample reaction vials, both after equilibration.  $[\text{Sample}]$  is the weight concentration of the samples (in grams/mL). The  $[\text{HMD}]_{\text{gain}}$  was multiplied by two because two molecules of TMCS react to form one molecule of HMD. For an accurate water correction using HMD, it was important to maintain a low water content on the samples.

The precision of the TMCS uptake for the dual phase filler was estimated to be 0.007 mmole/g ( $1\sigma$ ) and for the silica sample 0.037 mmole/g ( $1\sigma$ ).

#### LiAlH<sub>4</sub>

Samples were dried for 16 hours at 150 °C in an oven contained in a dry box. All weighing and reagent transfers were conducted in a dry box. The conditions of the dry box were the same as those described in the TMCS procedure. The sample was weighed into the reaction vessel, the amount depending on the expected hydrogen generated from the sample. To a separate side arm vessel, 20 mL of 0.5 M LiAlH<sub>4</sub> in 2-ethoxy 2-ethylether was added. The side arm vessel was then attached to the reaction vessel and the assembly was closed to the atmosphere with a vacuum valve. The assembly was taken out of the dry box and mounted on a glass apparatus used to measure the volume of hydrogen evolved, a modified version of that described by Colson.<sup>34</sup> This glass apparatus was equipped with a pump and an argon gas supply so as to maintain the necessary dry atmosphere for this reaction. The reaction was commenced by transferring the contents of the side arm vessel to the reaction vessel. Reactions were carried out at ambient conditions. The volume of hydrogen evolved was converted to STP and then to moles of hydrogen evolved per gram of sample.

#### pH

The pH of an aqueous slurry of the samples was obtained by following ASTM D 1512 (Volume 09.01) Test Method A, with the modification of the sample concentration, 2 grams of sample in 50 mL of water.

## ESTIMATE OF THE SILICA PHASE SURFACE AREA

We found that iodine does not adsorb onto silica when using the ASTM D 1510 method for iodine number on carbon black. Nitrogen adsorbs onto both carbon and silica surfaces. This means that the adsorption of iodine can be used as an estimate of the carbon phase surface area in the dual phase fillers, assuming that 1 mg/g of iodine adsorbed is equivalent to 1 m<sup>2</sup>/g of surface area as in the case of furnace carbon blacks. We modified the ASTM method such that the amount of sample used was varied to maintain a constant amount of iodine adsorbed, about 90 mg, a result of the ASTM method not being located on the flat portion of the isotherm. All samples, prior to iodine adsorption, were Soxhlet extracted for 24 hours with toluene and dried at 125 °C for 2 hours. The difference between nitrogen surface area and iodine number was then an estimate of the silica phase surface area.

## TREATED SAMPLES

Hydrofluoric and nitric acid treatments were conducted as discussed in Part III.<sup>3</sup> After nitric acid treatment, the samples were Soxhlet extracted, as described in Part III, to remove residual nitric acid from the fillers. Water treatment was done by Soxhlet extracting the samples with water for 72 hours.

## INFRARED SPECTROSCOPY

Infrared spectra were obtained in accordance with the procedure described in Part III.<sup>3</sup>

## RESULTS AND DISCUSSION

## TMCS UPTAKE

As previously mentioned, TMCS was chosen as an analytical probe to estimate the amount of functional groups available to react with organosilane coupling agents, such as TESPT.

**Silica.**—The amount of TMCS uptake with the fumed silica was found to be 0.819 mmoles/g (1.6 groups/nm<sup>2</sup>), see Table II. This is in reasonable agreement with 0.77 mmoles/g of trimethylsilyl groups attached to the surface of the same type and grade of silica, using hexamethyldisilazane, found by Chmielowiec.<sup>12</sup> Morrow and McFarlan,<sup>35</sup> using hexamethyldisilazane in a gas phase reaction with the same fumed silica, found there were 1.42 silanol groups/nm<sup>2</sup> available to react with a trimethylsilyl group, which translates to 0.75 mmoles/g. The reason for the amount of TMCS uptake reported herein being higher than the literature values may be a result of longer reaction times, the use of an amine catalyst and TMCS being a smaller molecule than hexamethyldisilazane.

Maciel<sup>36</sup> determined that the maximum lateral extension of the trimethylsilyl group on the surface of silica is approximately 0.37 nm (a full width of 0.74 nm) which should result in a projected area occupied by the trimethylsilyl group of 0.43 nm<sup>2</sup>, based on close-packing. This translates to an approximate maximum packing density of the trimethyl groups onto a surface of about 2.1/nm<sup>2</sup>. However, if a spherical close packing scheme is considered, then the projected area of the trimethylsilyl group drops to approximately 0.32 nm<sup>2</sup>, translating to a maximum trimethylsilyl packing density of 2.8/nm<sup>2</sup>. Nakamura<sup>26</sup> using trimethylchlorosilane found the maximum packing density of trimethylsilyl groups attached to a silica surface was 2.48/nm<sup>2</sup>, in the middle of the range suggested by Maciel. We observed that longer reaction times between TMCS and a silica surface results in an increase in the TMCS uptake. For example, when the fumed silica was treated with TMCS for 88 hours instead of 16 hours, the TMCS uptake increased to 0.975 mmoles/g or 1.85 trimethylsilyl groups/nm<sup>2</sup>. Perhaps this is a result of the packing issues described by Maciel, as previously discussed.

**Dual phase fillers.**—The TMCS uptake for the dual phase fillers is listed in Table II. The TMCS uptake is less for the dual phase fillers than silica (per unit mass), but more than for carbon black (N234 and N134). In fact the amount of TMCS uptake was so small on these carbon blacks it can be considered relatively insignificant. From this, it was postulated that on conventional furnace grade carbon blacks, the concentration of functional groups available to react with organosilane



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coupling agents is very low in comparison to either silica or the dual phase fillers. The TMCS uptake on dual phase fillers increased with silicon content and surface area. Comparing the TMCS uptake of the dual phase fillers with conventional carbon black suggests that the predominant functional group responsible for the TMCS uptake on the dual phase fillers is silanol, assuming that the carbon phase on the dual phase fillers is similar to carbon black.

Carbon black, however, can be made more reactive towards TMCS by oxidation, for example with nitric acid. As can be seen in Table II, oxidized carbon blacks  $\text{HNO}_3$ -N234 and Carbon A, have measurably more TMCS uptake than conventional carbon blacks. Nitric acid treatment places oxygen groups, in particular carboxylic acid groups, onto carbon blacks and carbon-silica dual phase fillers as shown in part three of this series of papers<sup>3</sup> and substantiated by the low pH of these treated samples, as can be seen in Table II. This increase in TMCS uptake with oxidized carbon blacks indicates that it is possible for carbon phase oxygen groups to participate in the uptake of TMCS. It is informative that nitric acid treatment adds more functional groups to the dual phase filler than to carbon black. This was illustrated by comparing the difference in TMCS uptake of  $\text{H}_2\text{O}$ -N234 versus  $\text{HNO}_3$ -N234 (a difference of 0.01 mmole/g) and  $\text{H}_2\text{O}$ -CSDPF-A versus  $\text{HNO}_3$ -CSDPF-A (a difference of 0.03 mmole/g), see Table II. The comparison of the nitric acid treatment was made against the water Soxhlet extracted carbon black, because the samples treated with nitric acid were subsequently water Soxhlet extracted. This comparison revealed that nitric acid treatment adds 3 times the amount of functional groups that can participate in the TMCS uptake onto CSDPF-A than onto N234.

Surprisingly, removing the silica phase from CSDPF-A by treatment with hydrofluoric acid ( $\text{HF}$ -CSDPF-A) resulted in a TMCS uptake significantly above that of N234 and N234 treated with  $\text{HF}$  (0.009 mmole/g). Considering that the silicon remaining was very low and probably unavailable to the TMCS molecule, suggests that some fraction of the carbon phase contains functional groups that can react with TMCS. Presumably the carbon phase functional groups that react with TMCS, after  $\text{HF}$  treatment, are hidden by the silica phase in the CSDPF-A and made available only upon removal of the silica phase. A more mild removal of the silica phase can be accomplished by Soxhlet extracting the dual phase fillers with water, for example  $\text{H}_2\text{O}$ -CSDPF-A. This can be accomplished because silica is slightly soluble in hot water, and the dissolution can be enhanced by the continuous supply of pure water by employing a Soxhlet apparatus. The silicon

TABLE II  
COMPARISON OF TMCS UPTAKE, ACTIVE HYDROGEN AND pH

Samples <sup>a</sup>	TMCS Uptake, mmole/g	TMCS Uptake, <sup>b</sup> groups/nm <sup>2</sup>	Active Hydrogen, mmole/g	Active Hydrogen, <sup>b</sup> groups/nm <sup>2</sup>	pH
CSDPF-A	0.081	0.32	0.494	1.93	5.89
CSDPF-E	0.107	0.31	0.514	1.47	5.72
CSDPF-F	0.048	0.28	0.370	2.17	6.72
N234	0.003	0.01	0.133	0.66	7.53
N134	0.000	0.00	0.185	0.65	8.10
$\text{HNO}_3$ -CSDPF-A	0.072	0.18	0.850	2.09	3.39
$\text{HNO}_3$ -N234	0.012	0.05	0.462	1.78	3.38
$\text{H}_2\text{O}$ -CSDPF-A	0.042	0.11	0.359	0.92	6.22
$\text{H}_2\text{O}$ -N234	0.001	0.005	0.125	0.62	7.72
Carbon A	0.047	0.05	—	—	3.36
$\text{HF}$ -CSDPF-A	0.059	0.11	—	—	—
Silica	0.819	1.6	1.59	3.01	4.42

<sup>a</sup>  $\text{HNO}_3$ -CSDPF-A is nitric acid treated CSDPF-A.  $\text{HNO}_3$ -N234 is nitric acid treated N234.  $\text{H}_2\text{O}$ -CSDPF-A is water Soxhlet extracted CSDPF-A.  $\text{H}_2\text{O}$ -N234 is water Soxhlet extracted N234. Carbon A is BLACK PEARLS<sup>®</sup> 1400, a commercial nitric acid treated carbon black having a nominal surface area of 560 m<sup>2</sup>/g. For TMCS uptake sample was used as is, but water Soxhlet extracted for pH measurement. BLACK PEARLS<sup>®</sup> is a registered trademark of Carbot Corporation.

<sup>b</sup> Calculated based on BET nitrogen surface area.

content on the water extracted dual phase filler A was lower and accordingly the TMCS uptake was lower than the CSDPF-A. The H<sub>2</sub>O-CSDPF-A had more silica and lower TMCS uptake than HF-CSDPF-A. This, perhaps, indicates that partial removal of the silica phase reduces the surface silanol content, but does not expose all of the carbon phase functional groups that can participate in the TMCS uptake.

The ratio of TMCS uptake to surface area was lower on the dual phase fillers than silica, as listed in Table II. For example, CSDPF-A has a TMCS packing density of 0.32/nm<sup>2</sup>, whereas the fumed silica sample has a packing density of 1.6/nm<sup>2</sup>. The lower TMCS uptake packing density for the dual phase fillers compared to silica is likely a result of the carbon phase either not participating or participating only in a limited amount in the TMCS uptake and therefore the surface area used to calculate the packing density (BET nitrogen surface area which is a measure of silica phase and carbon phase surface areas) is inappropriate for the dual phase fillers. To compare the trimethylsilyl packing density of dual phase fillers to silica requires a silica phase surface area estimate for the dual phase fillers.

As with the silica sample, we have found that the TMCS uptake of CSDPF-A increases with longer reaction times while carbon black N234 is unaffected. For example, equilibrating CSDPF-A and N234 with TMCS for 88 hours instead of 16 hours increased the TMCS uptake of CSDPF-A to 0.093 mmole/g and N234 remained the same at 0.003 mmole/g. This increase in TMCS uptake for the dual phase filler may be a result of the packing issues previously discussed.

#### LiAlH<sub>4</sub>

Lithium aluminum hydride (LiAlH<sub>4</sub>) has been used for a number of years as a measure of active hydrogen.<sup>34,37</sup> Functional groups containing active hydrogens that liberate hydrogen upon equilibration with LiAlH<sub>4</sub> include: alcohols, phenols, carboxylic acids, silanols, water, etc. This reaction has been used on carbon black for a number of years as a measure of the total active hydrogen content.<sup>38</sup> LiAlH<sub>4</sub> is also used to measure the total silanol content of silicas.<sup>9</sup> Lithium aluminum hydride, although a powerful reducing agent, reacts with a number of functional groups (e.g., ketones, aldehydes, quinones and lactones), but does not liberate hydrogen unless there is excess water present.<sup>39</sup>

Table II contains the active hydrogens measured on the dual phase fillers, carbon blacks, silica and treated samples. The active hydrogen content for carbon blacks are higher than anticipated considering the very small amount of TMCS uptake and there are no detectable phenolic and carboxylic acid functional groups, based on no measurable infrared band in the 1250 and 1700 cm<sup>-1</sup> regions, respectively.<sup>3</sup> One possible explanation is there may be water still trapped in micropores or as water of hydration associated with functional groups,<sup>40,41</sup> even after drying at 150 °C under an argon flow for 16 hours. This is supported by Rivin<sup>42</sup> who found that carbon blacks evolve water up to 400 °C. Because CO<sub>2</sub> begins to evolve at 200 °C, presumably due in part to decomposition of carbon-oxygen functional groups,<sup>43</sup> and silanols may condense at temperatures higher than 170 °C,<sup>44</sup> the samples were dried at 150 °C to minimize removal of these groups.

The active hydrogen content of the dual phase fillers increases as the TMCS uptake increases, as shown in Table II. The ratio of TMCS uptake to active hydrogen content is lower in the dual phase fillers (0.1 to 0.2) than for silica (0.5). This is probably a result of hydrated water and water in the micropores generating artificially high active hydrogen content on the dual phase fillers, steric hindrance of the TMCS molecule relative to LiAlH<sub>4</sub>, and perhaps differences in reactivity between TMCS and LiAlH<sub>4</sub> with the carbon phase functional groups.

It is not surprising that the amount of TMCS uptake would be less than the total silanol content on silicas (as measured by LiAlH<sub>4</sub>) based on steric considerations. Morrow and McFarlan<sup>35</sup> measured the total silanol content of the same grade of fumed silica used in our work to be 3.1 SiOH groups/nm<sup>2</sup> which translates to 1.65 mmole/g using a BET surface area of 320 m<sup>2</sup>/g. The total silanol content was determined by a combination of mass loss upon heating from 150 to 450 °C and exchange with D<sub>2</sub>O. The ratio of the uptake of trimethylsilyl groups to total silanols is calculated to be 0.45. This ratio is in reasonable agreement with our findings of 0.53 for the same silica.

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## pH

The pH of carbon black slurries is a classical test for surface acidity, dependent on functional groups containing acidic protons. Although the pH of an aqueous slurry of powders can be influenced by impurities, the pH of carbon black is still measured.<sup>45</sup> The pH can also be influenced by the aromatic character of the surface, where the surface can  $\pi$  complex with the protons resulting in a more basic pH. Consequently, using pH to estimate silanol content is equivocal due to some of these interferences. In spite of this, there is a general inverse relationship between strong acid content of carbon black and pH.<sup>38</sup> The pH of silica slurries is expected to be acidic because the silanols on the surface of silica are slightly acidic having a  $pK_a$  of approximately 6.5.<sup>46</sup>

Table II contains the pH of the dual phase fillers, carbon blacks, silica and treated samples. As expected the carbon black samples are near neutral and the fumed silica is acidic. The pH of the dual phase fillers is inversely related to the silicon content, the TMCS uptake, and the amount of active hydrogens. Treatment of carbon black and the dual phase fillers with nitric acid reduces the pH, a result of the formation of carboxylic acid groups.

## AVAILABLE REACTIVE GROUP DENSITIES

Since TMCS does not react appreciably with carbon black, and the TMCS uptake is reduced upon mild dissolution of the silica phase of CSDPF-A, it is presumed that the reactive groups responsible for the uptake of TMCS are predominately silanol groups. Because the dual phase fillers consist of a silica phase and a carbon phase, the amount of TMCS uptake cannot be readily converted into silanol groups per unit area. To obtain the surface area of each phase, it is necessary to have a method that uses adsorbates that selectively adsorb onto the surface of the different phases. As mentioned in the experimental section, the iodine number can be used as a measure of the carbon phase surface area, and the difference between nitrogen surface area and iodine number can be used as a rough estimate of the silica phase surface area.

There are some limitations, however, with this scheme. Iodine, in addition to physical adsorption onto carbon surfaces, is consumed by electrochemical reduction by the  $\pi$  electrons in the aromatic basal plane.<sup>42</sup> Also, surface impurities such as oxygen and sulfur groups<sup>47</sup> as well as adsorbed hydrocarbons can affect the iodine number. Since iodine is bigger than nitrogen, the pore size distribution of the sample can furthermore influence the difference between iodine number and nitrogen surface area.<sup>48,49</sup> Despite these interferences, the agreement between iodine number and nitrogen surface area is good, for moderate surface area furnace carbon blacks.<sup>50,51</sup> To convert iodine number into carbon phase surface area, 1  $m^2/g$  of surface is presumed to adsorb 1 mg/g of iodine.<sup>52</sup>

The surface areas of the carbon and silica phases have been estimated for the dual phase fillers, using the scheme previously described, and can be found in Table III. The carbon phase surface area estimate may be on the low side, as a result of suspected increase in carbon phase oxygen groups on the dual phase fillers relative to carbon black.<sup>3</sup> This results in an underestimate of the carbon phase surface area generating an overestimate of the silica phase surface area and consequently a decrease in the estimated trimethylsilyl packing densities.

The trimethylsilyl packing density for the silica sample is 1.6 groups/ $nm^2$ , whereas, the packing density on the silica phase of the dual phase filler is about 1 trimethylsilyl group/ $nm^2$ . This

TABLE III  
ESTIMATE OF CARBON AND SILICA PHASE SURFACE AREAS ON CARBON-SILICA DUAL PHASE FILLERS

Sample	BET $N_2$ SA, $m^2/g$	Iodine Number, mg/g	Carbon Phase Surface Area, $m^2/g$	Silica Phase Surface Area, $m^2/g$	TMCS Uptake Silica Phase, <sup>a</sup> groups/ $nm^2$
CSDPF-A	154.3	102.2	102	52	0.94
CSDPF-E	210.8	130.2	130	81	0.80
CSDPF-F	102.6	81.6	82	21	1.4

<sup>a</sup> TMCS uptake (groups/ $nm^2$ ) is based on the estimated silica phase surface area.

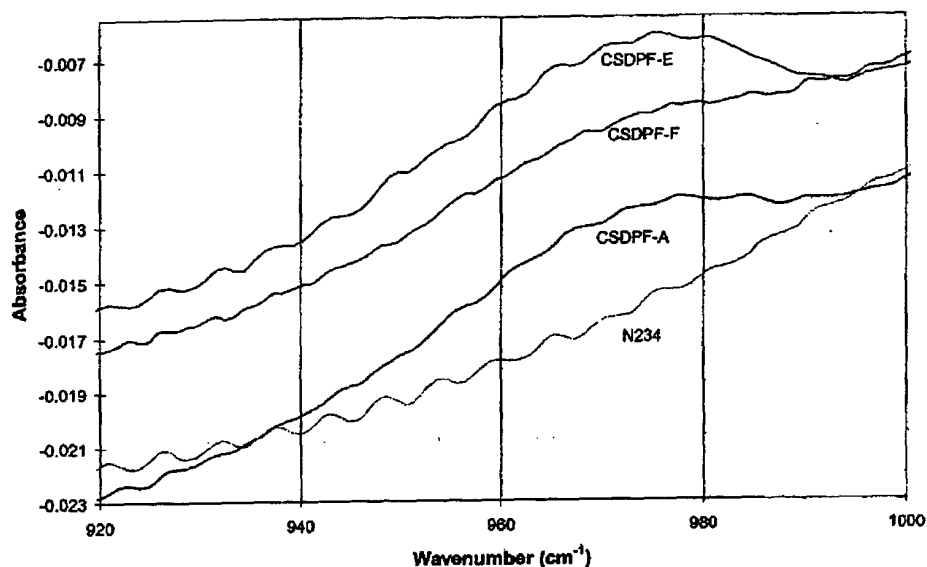


FIG. 2.—Low wavenumber infrared spectra of carbon black and dual phase fillers.

packing density estimate for the dual phase fillers is lower than silica; probably as a result of the overestimate of the silica phase surface area. For more accurate packing densities, perhaps other methods of measuring the surface areas of the individual phases should be investigated.<sup>53</sup>

#### SPECTROSCOPY

As stated in the introduction section, infrared spectroscopy has been used to measure silanols on silica surfaces. In the case of the dual phase fillers, the IR region above  $3000\text{ cm}^{-1}$ , at this juncture, is not useful for silanol determinations, due to the large water band interfering with the silanol bands. We have observed, however, a band in the  $960$  to  $980\text{ cm}^{-1}$  region for both precipitated silica (not shown) and the dual phase filler. Ishida assigned the  $970\text{ cm}^{-1}$  band of fumed silica to the Si-O stretching mode of surface silanols.<sup>54</sup> Morrow claims that the band near  $975\text{ cm}^{-1}$  is due to the stretching mode of isolated silanols.<sup>15</sup> On the other hand, Tripp claims that the band at  $973\text{ cm}^{-1}$  is due to both isolated and geminal silanols.<sup>33</sup> Surprisingly this band is barely detectable for the fumed silica sample. The IR spectra of the  $975\text{ cm}^{-1}$  region is shown in Figure 2 for the dual phase fillers and carbon black N234. Note that the dual phase fillers

TABLE IV  
COMPARISON OF TMCS UPTAKE WITH IR ABSORBANCES AT  $975\text{ cm}^{-1}$  OF THE CARBON-SILICA DUAL PHASE FILLERS BEFORE AND AFTER REACTION WITH TMCS

Sample	TMCS Uptake, mmole/g	Before TMCS Absorbance @ $975\text{ cm}^{-1}$	After TMCS Absorbance <sup>a</sup> @ $975\text{ cm}^{-1}$
CSDPF-A	0.081	0.0029	0.0006
CSDPF-E	0.107	0.0036	0.0014
CSDPF-F	0.048	0.0015	0.0004

<sup>a</sup> As mentioned in the text, the peak remaining after reaction with TMCS is slightly shifted to lower wavenumbers.

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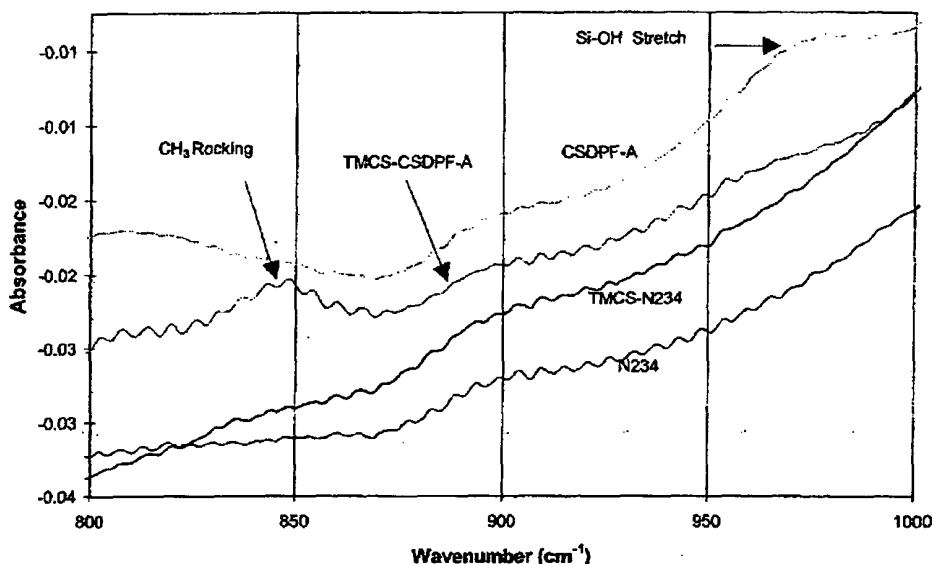


FIG. 3.—Comparison of low wavenumber infrared spectra of carbon-silica dual phase fillers and carbon black before and after treatment with TMCS.

contain a peak in the  $975\text{ cm}^{-1}$  region, consistent with the location of silanols, and carbon black is devoid of this peak.

A comparison of the infrared spectra of N234 and CSDPF-A before and after treatment with TMCS is given in Figure 3. Reacting the dual phase fillers with TMCS dramatically reduces the  $975\text{ cm}^{-1}$  band, shifts the residual band to lower wavenumbers by about 10 to  $15\text{ cm}^{-1}$ , and creates a band near the  $850\text{ cm}^{-1}$  region. This newly created band at  $850\text{ cm}^{-1}$  is a result of the  $\text{CH}_3$  rocking modes of the trimethylsilyl group on the surface.<sup>28</sup> Table IV contains the IR absorbance values at  $975\text{ cm}^{-1}$  before and after reaction with TMCS as well as the TMCS uptake amounts. These absorbance values were obtained by measuring the peak height above an interpolated baseline between approximately  $1000$  and  $920\text{ cm}^{-1}$ . A linear relationship between the absorbance values at  $975\text{ cm}^{-1}$  and TMCS uptake for the dual phase fillers and the silica sample is observed and is indicative of the involvement of the silanols in the uptake of TMCS. The loss in absorbance of the silanol band after reaction with TMCS supports the claim that TMCS is reacting with silanols on the surface of the dual phase fillers.

## CONCLUSIONS

It has been demonstrated that the carbon-silica dual phase fillers contain substantially more functional groups available to react with TMCS and  $\text{LiAlH}_4$  than carbon black. This is postulated as meaning that there are significantly more reactive functional groups on the dual phase fillers, depending on silicon content and surface area, available to react with silane coupling agents than on carbon black. Nitric acid treatment of carbon black and the dual phase filler results in an increase in the TMCS uptake, where the dual phase filler appears to be more susceptible to such oxidation. The significant TMCS uptake after removal of the silica phase from CSDPF-A suggests that there are carbon phase reactive functional groups present on the dual phase filler, perhaps under the silica phase. The trimethylsilyl packing density on the silica phase of the dual phase fillers has been estimated to be less than that of silica. This may be a result of an over estimate of the silica phase surface area using the iodine number and BET nitrogen surface area approach.

The active hydrogen content of the dual phase fillers, as measured by  $\text{LiAlH}_4$ , are higher than for carbon black, and increase with increasing silicon content. The pH of the dual phase fillers are more acidic than carbon black and decrease with increasing silanol content. The infrared work demonstrates that there are silanols, perhaps isolated silanols, present on the dual phase fillers. The reduction in the infrared band assigned to silanols after reaction with TMCS, provides evidence that there is a chemical reaction between TMCS and the surface silanols.

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**Modified carbon black**

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Publication date: 1985-08-08  
Inventor(s): USHIDA YOKO (JP); SUGIURA HIROSHI (JP)  
Applicant(s): TOYODA GOSEI KK (JP)  
Requested Patent: ☐ DE3502494  
Application Number: DE19853502494 19850125  
Priority Number(s): JP19840011885 19840127; JP19840149390 19840720  
IPC Classification: C09C1/48; C08K3/04; C08L21/00  
EC Classification: C08K3/00S, C08K3/04, C09C1/56, C08K9/02  
Equivalents:

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**Abstract**

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The invention relates to a modified carbon black, which comprises powdered carbon black and at least one metal compound, namely an oxide, sulphide, carbonate, phosphate, chloride, sulphate or nitrate of an element of Groups I to VI and VIII of the Periodic Table. The metal compound is added to the carbon black in an amount from 1 to 30 parts by weight per 100 parts by weight of powdered carbon black. The modified carbon black of the invention has excellent dispersibility in rubber. The rubber products obtained therefrom therefore have outstanding physical characteristics.



DE 2403545

Procedure for the production of FurnaceruSen with lowered  
Federal Post Office number the invention concerns a procedure  
for the production of Furnaceruss with lowered it Federal Post  
Office number under addition of structure-lowering additives.  
With that and in many variants accomplished  
Pumacerussverfahren actually admitted amplifier and color  
Russian of usually liquid hydrocarbons in a fireproof brick-lined  
flow reactor is made. Except the employment hydrocarbon  
generally from economic considerations still another gaseous  
fuel (natural gas, town gas) is given to the reactor. This gaseous  
fuel forms a hot flame out, into which the employment  
hydrocarbon (soot raw material) together with combustion air is  
injected usually in finely divided form. For the fine distribution of  
the soot raw material one avails oneself frequently the 2-  
Stoffserstaeu bung, whereby generally compressed air is used  
as atomizer medium. The finely divided soot raw material is  
generally somewhat downstream continued to interfere into the  
hot exhaust gases of the gaseous fuel flame, whereby it by  
pyrolysis and partial burn in soot and exhaust gas are  
converted. Before the soot exhaust mixture leaves and to the  
separating plant is supplied the reactor, it is cooled down by  
injecting water on a temperature under 9000C.